Supporting Information

How Beneficial is the *Explicit* Account of Doubly-Excited Configurations in Linear Response Theory?

Yevhen Horbatenko,[†] Seunghoon Lee,[‡] Michael Filatov,[*,†] and Cheol Ho Choi[*,†]

†*Department of Chemistry, Kyungpook National University, Daegu 702-701, South Korea*

‡*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

E-mail: mike.filatov@gmail.com; cchoi@knu.ac.kr

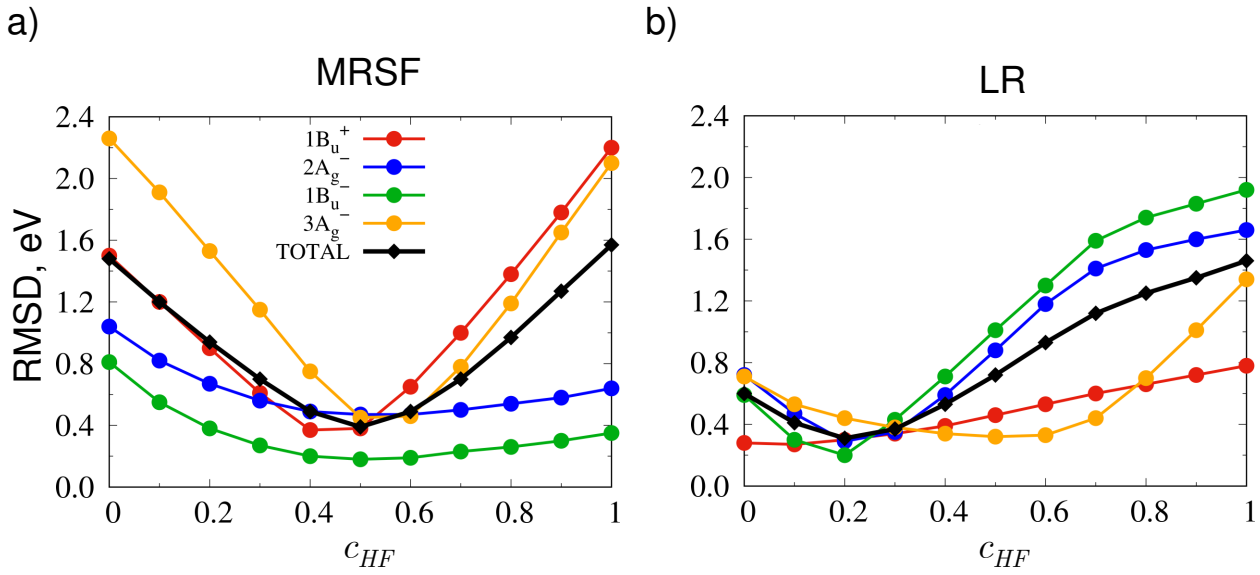

Figure S1: Dependence of the RMSD of the vertical excitation energies on the amount of the exact exchange c_{HF} obtained with the (a) MRSF and (b) LR methods, by employing $B(1 - c_{HF})HF(c_{HF})$ functionals, for $1B_u^+$, $2A_g^-$, $1B_u^-$, and $3A_g^-$ exited states. The total RMSD over all the excited states is shown as well.

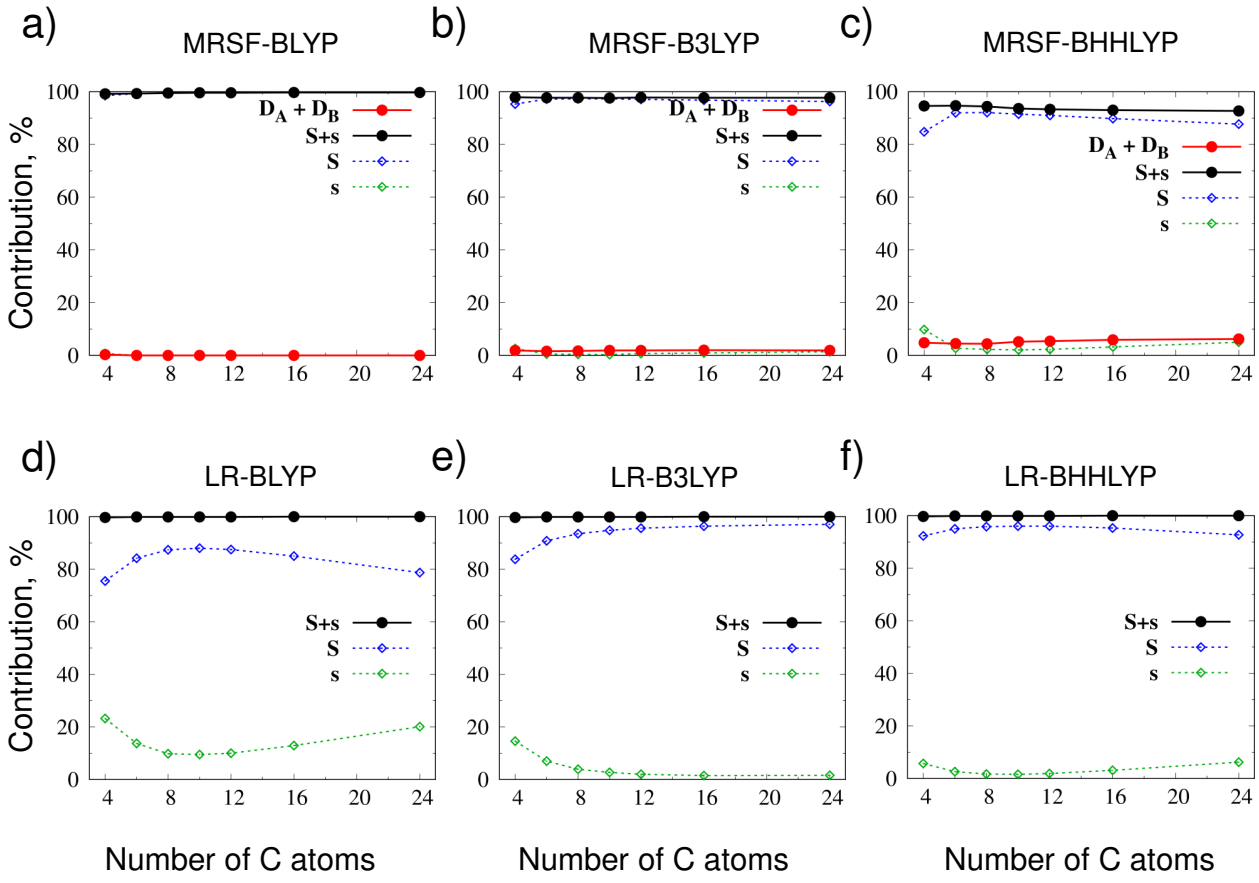

Figure S2: Contribution of various excited configurations to the $1B_u^+$ excited state obtained with (a)-(c) MRSF and (d)-(f) LR. '**s**' stands for minor singly-excited configurations, not classified here.

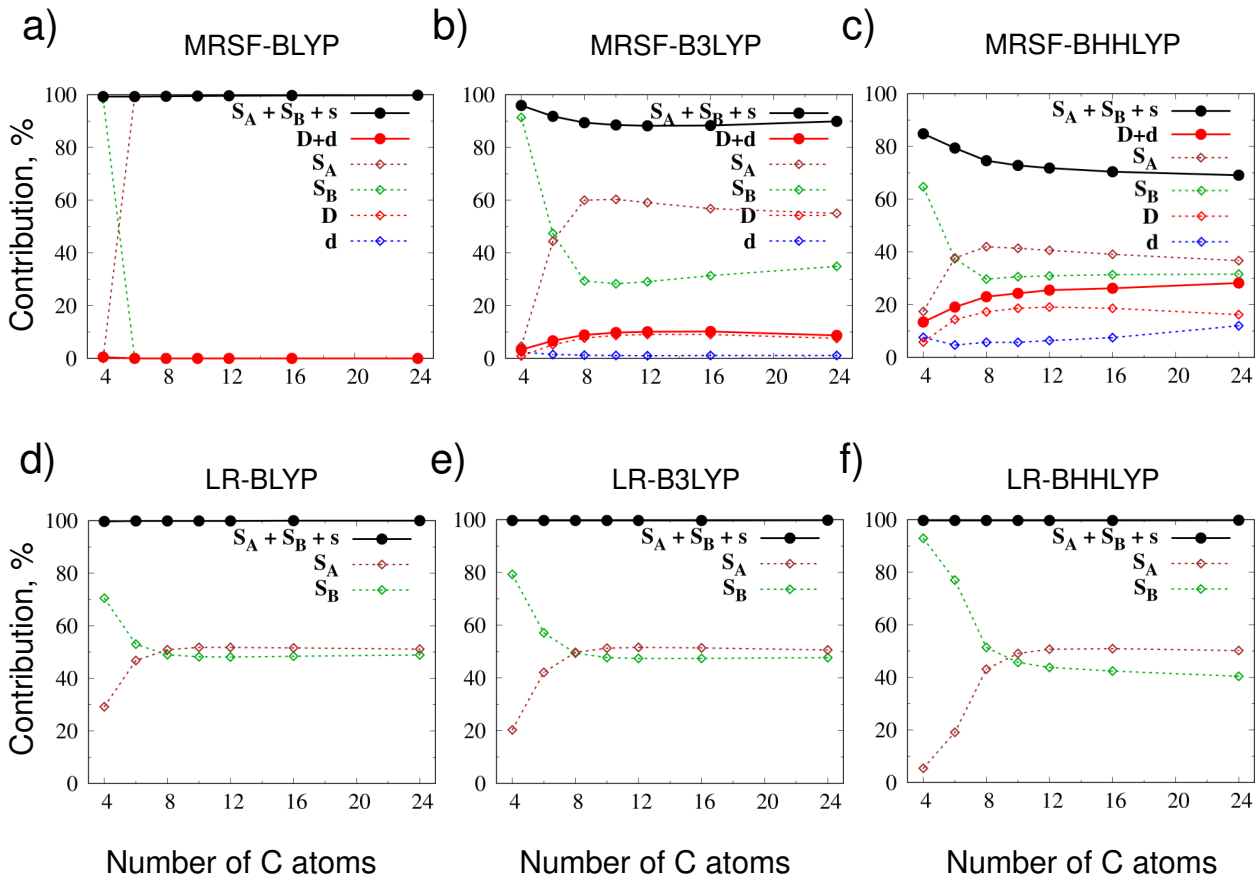

Figure S3: Contribution of various excited configurations to the $2A_g^-$ excited state obtained with (a) MRSF and (b) LR. '**s**' and '**d**' stand for minor singly- and doubly-excited configurations, respectively, not classified here

Table S1: Comparison of the optimized coupled-cluster geometries for C_4H_6 (CC3/aug-cc-pVTZ, from ref 56 in the main text) and C_6H_8 (CCSD(T)/aug-cc-pVTZ, from ref 56 in the main text) with those from MP2/6-31G* (from ref 59 in the main text). The difference in C–C bond distances (in Å) was calculated as $\Delta_{CC} = d_{CC}(\text{MP2}) - d_{CC}(\text{couple-cluster})$.

Polyene	$\Delta_{C=C}$ (terminal)	Δ_{C-C}	$\Delta_{C=C}$ (middle)
C_4H_6	0.004	0.005	-
C_6H_8	0.005	0.003	0.008

Cartesian Coordinates (in bohr) of Benchmark Molecules

Table S2: Cartesian coordinates (in Å) of the ground state geometries.

atom	charge	x	y	z
Butadiene (C4H6). Taken from Ref 43 in the main text.				
C	6.0	1.1465624400	0.0000000000	0.7546882000
C	6.0	-1.1465624400	0.0000000000	-0.7546882000
C	6.0	3.4813264700	0.0000000000	-0.2248280500
C	6.0	-3.4813264700	0.0000000000	0.2248280500
H	1.0	0.9077097800	0.0000000000	2.7888392500
H	1.0	-0.9077097800	0.0000000000	-2.7888392500
H	1.0	3.7752581400	0.0000000000	-2.2489547000
H	1.0	-3.7752581400	0.0000000000	2.2489547000
H	1.0	5.1366496700	0.0000000000	0.9686189000
H	1.0	-5.1366496700	0.0000000000	-0.9686189000
Hexatriene (C6H8). Taken from Ref 43 in the main text.				
C	6.0	-0.0002476000	1.2717818000	0.0000000000
C	6.0	0.0002476000	-1.2717818000	0.0000000000

C	6.0	2.2709215000	2.7978697000	0.0000000000
C	6.0	-2.2709215000	-2.7978697000	0.0000000000
C	6.0	2.2709215000	5.3313687000	0.0000000000
C	6.0	-2.2709215000	-5.3313687000	0.0000000000
H	1.0	-1.7938035000	2.2677902000	0.0000000000
H	1.0	1.7938035000	-2.2677902000	0.0000000000
H	1.0	4.0548550000	1.7921594000	0.0000000000
H	1.0	-4.0548550000	-1.7921594000	0.0000000000
H	1.0	0.5178662000	6.3842559000	0.0000000000
H	1.0	-0.5178662000	-6.3842559000	0.0000000000
H	1.0	4.0110587000	6.3968755000	0.0000000000
H	1.0	-4.0110587000	-6.3968755000	0.0000000000

Octatetraene (C8H10). Taken from Ref 46 in the main text.

HYDROGEN	1.0	1.8355437642	2.3057321545	0.0000000000
HYDROGEN	1.0	-1.8355437642	-2.3057321545	0.0000000000
HYDROGEN	1.0	3.9648151957	-1.8608490849	0.0000000000
HYDROGEN	1.0	-3.9648151957	1.8608490849	0.0000000000
HYDROGEN	1.0	0.2775705120	-6.4600377339	0.0000000000
HYDROGEN	1.0	-0.2775705120	6.4600377339	0.0000000000
HYDROGEN	1.0	4.1450629296	-9.0065965701	0.0000000000
HYDROGEN	1.0	-4.1450629296	9.0065965701	0.0000000000
HYDROGEN	1.0	6.0956853373	-6.1047616912	0.0000000000
HYDROGEN	1.0	-6.0956853373	6.1047616912	0.0000000000
CARBON	6.0	0.0000000000	1.3634335207	0.0000000000
CARBON	6.0	0.0000000000	-1.3634335207	0.0000000000

CARBON	6.0	2.1259795288	-2.7958930606	0.0000000000
CARBON	6.0	-2.1259795288	2.7958930606	0.0000000000
CARBON	6.0	2.1185283392	-5.5346521477	0.0000000000
CARBON	6.0	-2.1185283392	5.5346521477	0.0000000000
CARBON	6.0	4.2280502463	-6.9585039857	0.0000000000
CARBON	6.0	-4.2280502463	6.9585039857	0.0000000000

Decapentaene (C10H12). This work.

CARBON	6.0	10.4746182750	-0.3527899549	0.0000000000
CARBON	6.0	-10.4746182750	0.3527899549	0.0000000000
HYDROGEN	1.0	10.7519827501	1.6822051222	0.0000000000
HYDROGEN	1.0	-10.7519827501	-1.6822051222	0.0000000000
HYDROGEN	1.0	12.1603243268	-1.5196072519	0.0000000000
HYDROGEN	1.0	-12.1603243268	1.5196072519	0.0000000000
CARBON	6.0	8.1405497789	-1.3745483141	0.0000000000
CARBON	6.0	-8.1405497789	1.3745483141	0.0000000000
HYDROGEN	1.0	7.9386848901	-3.4254073636	0.0000000000
HYDROGEN	1.0	-7.9386848901	3.4254073636	0.0000000000
CARBON	6.0	5.8303685340	0.0966235697	0.0000000000
CARBON	6.0	-5.8303685340	-0.0966235697	0.0000000000
HYDROGEN	1.0	6.0224789620	2.1508722229	0.0000000000
HYDROGEN	1.0	-6.0224789620	-2.1508722229	0.0000000000
CARBON	6.0	3.4789437338	-0.9357912866	0.0000000000
CARBON	6.0	-3.4789437338	0.9357912866	0.0000000000
HYDROGEN	1.0	-3.2960334372	2.9914089836	0.0000000000
HYDROGEN	1.0	3.2960334372	-2.9914089836	0.0000000000

CARBON	6.0	1.1767251716	0.5190201867	0.0000000000
CARBON	6.0	-1.1767251716	-0.5190201867	0.0000000000
HYDROGEN	1.0	1.3571728044	2.5747966606	0.0000000000
HYDROGEN	1.0	-1.3571728044	-2.5747966606	0.0000000000

Dodecahexaene (C12H14). This work.

CARBON	6.0	12.7853310053	-0.8595391840	0.0000000000
CARBON	6.0	-12.7853310053	0.8595391840	0.0000000000
HYDROGEN	1.0	13.1114625619	1.1682171633	0.0000000000
HYDROGEN	1.0	-13.1114625619	-1.1682171633	0.0000000000
HYDROGEN	1.0	14.4424784247	-2.0665654099	0.0000000000
HYDROGEN	1.0	-14.4424784247	2.0665654099	0.0000000000
CARBON	6.0	10.4270034207	-1.8249461015	0.0000000000
CARBON	6.0	-10.4270034207	1.8249461015	0.0000000000
HYDROGEN	1.0	10.1762021756	-3.8704200661	0.0000000000
HYDROGEN	1.0	-10.1762021756	3.8704200661	0.0000000000
CARBON	6.0	8.1533748270	-0.2992126234	0.0000000000
CARBON	6.0	-8.1533748270	0.2992126234	0.0000000000
HYDROGEN	1.0	8.3942455186	1.7499021875	0.0000000000
HYDROGEN	1.0	-8.3942455186	-1.7499021875	0.0000000000
CARBON	6.0	5.7769146451	-1.2755337157	0.0000000000
CARBON	6.0	-5.7769146451	1.2755337157	0.0000000000
HYDROGEN	1.0	5.5459200489	-3.3263723158	0.0000000000
HYDROGEN	1.0	-5.5459200489	3.3263723158	0.0000000000
CARBON	6.0	3.5116413899	0.2320006485	0.0000000000
CARBON	6.0	-3.5116413899	-0.2320006485	0.0000000000

HYDROGEN	1.0	-3.7392156822	-2.2831526369	0.0000000000
HYDROGEN	1.0	3.7392156822	2.2831526369	0.0000000000
CARBON	6.0	1.1318278570	-0.7516676965	0.0000000000
CARBON	6.0	-1.1318278570	0.7516676965	0.0000000000
HYDROGEN	1.0	0.9059306455	-2.8031599471	0.0000000000
HYDROGEN	1.0	-0.9059306455	2.8031599471	0.0000000000

Hexadecaoctaene (C16H18). This work.

CARBON	6.0	3.0843497532	17.2084874266	0.0000000000
CARBON	6.0	-3.0843497532	-17.2084874266	0.0000000000
HYDROGEN	1.0	5.1287057010	17.0115876696	0.0000000000
HYDROGEN	1.0	-5.1287057010	-17.0115876696	0.0000000000
HYDROGEN	1.0	2.3352609644	19.1168653441	0.0000000000
HYDROGEN	1.0	-2.3352609644	-19.1168653441	0.0000000000
CARBON	6.0	1.5542029503	15.1704200155	0.0000000000
CARBON	6.0	-1.5542029503	-15.1704200155	0.0000000000
HYDROGEN	1.0	-0.4882537212	15.4448272864	0.0000000000
HYDROGEN	1.0	0.4882537212	-15.4448272864	0.0000000000
CARBON	6.0	2.4555870275	12.5855611755	0.0000000000
CARBON	6.0	-2.4555870275	-12.5855611755	0.0000000000
HYDROGEN	1.0	4.4990104993	12.3003399387	0.0000000000
HYDROGEN	1.0	-4.4990104993	-12.3003399387	0.0000000000
CARBON	6.0	0.9097271415	10.5323568007	0.0000000000
CARBON	6.0	-0.9097271415	-10.5323568007	0.0000000000
HYDROGEN	1.0	-1.1328349593	10.8280275421	0.0000000000
HYDROGEN	1.0	1.1328349593	-10.8280275421	0.0000000000

CARBON	6.0	1.7947112376	7.9611340373	0.0000000000
CARBON	6.0	-1.7947112376	-7.9611340373	0.0000000000
HYDROGEN	1.0	3.8366245248	7.6615187273	0.0000000000
HYDROGEN	1.0	-3.8366245248	-7.6615187273	0.0000000000
CARBON	6.0	0.2396850924	5.9058540134	0.0000000000
CARBON	6.0	-0.2396850924	-5.9058540134	0.0000000000
HYDROGEN	1.0	-1.8020776051	6.2080889570	0.0000000000
HYDROGEN	1.0	1.8020776051	-6.2080889570	0.0000000000
CARBON	6.0	1.1190279577	3.3390965279	0.0000000000
CARBON	6.0	-1.1190279577	-3.3390965279	0.0000000000
HYDROGEN	1.0	-3.1605739192	-3.0355840660	0.0000000000
HYDROGEN	1.0	3.1605739192	3.0355840660	0.0000000000
CARBON	6.0	-0.4389312631	1.2827835017	0.0000000000
CARBON	6.0	0.4389312631	-1.2827835017	0.0000000000
HYDROGEN	1.0	-2.4804408352	1.5869604956	0.0000000000
HYDROGEN	1.0	2.4804408352	-1.5869604956	0.0000000000

Tetracosadodecaene (C24H26). This work.

CARBON	6.0	1.1227246142	-0.7556040338	0.0000000000
CARBON	6.0	-1.1227246142	0.7556040338	0.0000000000
CARBON	6.0	26.6981523196	-2.5784921430	0.0000000000
CARBON	6.0	-26.6981523196	2.5784921430	0.0000000000
HYDROGEN	1.0	0.8884076008	-2.8064518322	0.0000000000
HYDROGEN	1.0	-0.8884076008	2.8064518322	0.0000000000
HYDROGEN	1.0	27.0404678927	-0.5533885597	0.0000000000
HYDROGEN	1.0	-27.0404678927	0.5533885597	0.0000000000

HYDROGEN	1.0	28.3455652584	-3.7987621773	0.0000000000
HYDROGEN	1.0	-28.3455652584	3.7987621773	0.0000000000
CARBON	6.0	3.5170298736	0.2160019341	0.0000000000
CARBON	6.0	-3.5170298736	-0.2160019341	0.0000000000
CARBON	6.0	24.3317874937	-3.5250183559	0.0000000000
CARBON	6.0	-24.3317874937	3.5250183559	0.0000000000
HYDROGEN	1.0	3.7515492381	2.2668121661	0.0000000000
HYDROGEN	1.0	-3.7515492381	-2.2668121661	0.0000000000
HYDROGEN	1.0	24.0648282794	-5.5685029614	0.0000000000
HYDROGEN	1.0	-24.0648282794	5.5685029614	0.0000000000
CARBON	6.0	5.7627683342	-1.2956319488	0.0000000000
CARBON	6.0	-5.7627683342	1.2956319488	0.0000000000
CARBON	6.0	22.0709317399	-1.9818481305	0.0000000000
CARBON	6.0	-22.0709317399	1.9818481305	0.0000000000
HYDROGEN	1.0	5.5279541724	-3.3464109724	0.0000000000
HYDROGEN	1.0	-5.5279541724	3.3464109724	0.0000000000
HYDROGEN	1.0	22.3275105743	0.0654130193	0.0000000000
HYDROGEN	1.0	-22.3275105743	-0.0654130193	0.0000000000
CARBON	6.0	8.1565027421	-0.3244783355	0.0000000000
CARBON	6.0	-8.1565027421	0.3244783355	0.0000000000
CARBON	6.0	19.6857230988	-2.9399003435	0.0000000000
CARBON	6.0	-19.6857230988	2.9399003435	0.0000000000
HYDROGEN	1.0	8.3917910352	1.7262098055	0.0000000000
HYDROGEN	1.0	-8.3917910352	-1.7262098055	0.0000000000
HYDROGEN	1.0	19.4397312000	-4.9890866266	0.0000000000
HYDROGEN	1.0	-19.4397312000	4.9890866266	0.0000000000

CARBON	6.0	10.4031743931	-1.8373526313	0.0000000000
CARBON	6.0	-10.4031743931	1.8373526313	0.0000000000
CARBON	6.0	17.4339403794	-1.4165561057	0.0000000000
CARBON	6.0	-17.4339403794	1.4165561057	0.0000000000
HYDROGEN	1.0	17.6756919473	0.6330530857	0.0000000000
HYDROGEN	1.0	-17.6756919473	-0.6330530857	0.0000000000
HYDROGEN	1.0	10.1671645291	-3.8879656999	0.0000000000
HYDROGEN	1.0	-10.1671645291	3.8879656999	0.0000000000
CARBON	6.0	12.7955875093	-0.8674302086	0.0000000000
CARBON	6.0	-12.7955875093	0.8674302086	0.0000000000
CARBON	6.0	15.0440387194	-2.3833750215	0.0000000000
CARBON	6.0	-15.0440387194	2.3833750215	0.0000000000
HYDROGEN	1.0	13.0327973555	1.1829454507	0.0000000000
HYDROGEN	1.0	-13.0327973555	-1.1829454507	0.0000000000
HYDROGEN	1.0	14.8051541546	-4.4335821063	0.0000000000
HYDROGEN	1.0	-14.8051541546	4.4335821063	0.0000000000